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"Nonstationary Time Series Analysis of Many-Body Dynamics"

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Nonstationary Time Series Analysis of Many-Body Dynamics

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A method for the analysis of computer simulations of ultrafast dynamical processes in many-body systems is presented, based on a joint time-frequency Wigner-Ville distribution calculated from the evolving particle velocities. This quantity has the interpretation of a time- and frequency- dependent effective temperature, and the evolution of the distribution allows dynamical information about energy flow between modes and relaxation mechanisms of many-body systems to be obtained. This approach is illustrated for the example of vibrational relaxation of an I_2 impurity in an argon cluster.

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Molecular dynamics simulation is an important theoretical approach to many problems in chemical physics, ranging from detailed studies of few-body reaction dynamics and intramolecular energy transfer [1] to the investigation equilibrium and nonequilibrium statistical mechanics in condensed matter systems [2]. A simulation is essentially a numerical experiment, however, and considerable data reduction of the often overwhelmingly detailed information generated by the calculation must be done before insight can be extracted. This analysis relies on a theoretical viewpoint to motivate the particular averaged quantities derived from the dynamical variables. For many-body condensed phase systems at or near equilibrium, statistical mechanics provides the appropriate formal foundation [3], and the data reduction accompanying molecular dynamics simulations involves calculating thermodynamic or statistical mechanical quantities, such as temperature, pressure, density, pair correlation functions, time correlation functions, and transport coefficients.

For few-body chemical dynamics in the gas phase, recent advances in nonlinear science have inspired novel approaches to the analysis of classical trajectory simulations, and have provided new insights into mechanisms of energy transfer and origins of statistical or nonstatistical behavior [4,5]. Systems with a small number of modes are now fairly well understood, although unsolved problems remain for systems with as few as three degrees of freedom [5]. Much less is known about dynamical processes in complex many-body systems and the nature of nonstatistical and mode-specific energy transfer mechanisms in large polyatomic molecules, van der Waals clusters, and condensed phases. The details of energy transfer in these systems are being revealed modern ultrafast optical experiments [6], stimulating the need for new theoretical approaches and insights.

In this brief report, we describe a method for the analysis of many-body molecular dynamics simulations, based on a novel application of joint time-

frequency approaches previously employed in nonstationary signal processing [7]. The method is based on a generalization of correlation function methodology of equilibrium statistical mechanics to the treatment of nonequilibrium and nonstatistical processes of importance in ultrafast phenomena.

Equilibrium statistical mechanics conceptually replaces dynamics with statistics, and thus views a complex many-body dynamical problem as a stochastic process with statistics characterized by time correlation functions. Such quantities can be related to spectroscopic and transport properties, and can often be measured directly by experiments [2,3]. An example is the velocity autocorrelation function of a "tagged" particle in a many-body system, given by:

$$c(t) = \frac{1}{3} \langle \vec{v}(0) \cdot \vec{v}(t) \rangle, \quad (1)$$

where the brackets indicate averaging over a statistical ensemble. For ergodic systems at equilibrium, the ensemble average can be replaced by a time average along a single trajectory:

$$c(t) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \frac{1}{3} \vec{v}(s) \cdot \vec{v}(t+s) ds \quad (2)$$

From the perspective of signal processing [7], the dynamics of a many-body system can be thought of as a stationary random process; the statistics of the process do not vary with time, thus allowing the time average to be computed.

Ultrafast dynamics in condensed phase systems driven by chemical reaction or optical excitation differ fundamentally from equilibrium or linear response regime processes. Initial conditions of extreme nonequilibrium nature are generated, and the following femtosecond and picosecond time scale processes can

exhibit nonstatistical, nondemocratic, and mode-specific energy relaxation pathways. This behavior cannot be thought of as a stationary process, and indeed, the particular sequences of events occurring in time and the underlying mechanisms governing them are of central importance.

To generalize the idea of a correlation function to ultrafast dynamical processes, nonstationary time series methods must be employed, and concepts such as evolutionary spectra [7,8] and time-dependent frequencies [5] must be utilized. Strictly, it is impossible to have complete knowledge of both the time dependence and frequency dependence of a signal, as the time-frequency uncertainty principle guarantees that these two types of information are incompatible. However, it is possible to define joint time-frequency distributions which balance the lack of certainty in a useful way. One example is the Wigner-Ville distribution [7,9]. This quantity is well-known in quantum mechanics [9], where, with the replacement of time and frequency by position and momentum, a phase space-like distribution, known as the Wigner function, is obtained.

We define the function $\Theta(t, \omega)$, which plays the role of a time- and frequency-dependent effective "temperature":

$$\Theta(t, \omega) = \frac{1}{2} \sum_{i=1}^N m_i \theta_i(t, \omega), \quad (3)$$

where m_i is the mass of atom i , and $\theta_i(t, \omega)$ is given by,

$$\theta_i(t, \omega) = \int_{-\infty}^{+\infty} \vec{v}_i(t - \tau/2) \cdot \vec{v}_i(t + \tau/2) e^{i\omega\tau} d\tau. \quad (4)$$

Under certain conditions, and after suitable averaging, this quantity can be related directly to conventional quantities in statistical mechanics [3]. By integrating over frequency, the instantaneous kinetic energy is obtained:

$$\frac{1}{2\pi} \int_{-\infty}^{+\infty} \Theta(t, \omega) d\omega = \frac{1}{2} \sum_{i=1}^N m_i \vec{v}_i(t) \cdot \vec{v}_i(t) = K(t) \quad (5)$$

Alternatively, for systems at equilibrium, an integration over time provides the spectral density of the mass-averaged velocity autocorrelation function:

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \Theta(t, \omega) dt = \frac{1}{2} \sum_{i=1}^N m_i \int_{-\infty}^{+\infty} \langle \vec{v}_i(0) \cdot \vec{v}_i(\tau) \rangle e^{i\omega\tau} d\tau \quad (6)$$

Integrating over both frequency and time yields a quantity that is proportional to the time-average kinetic energy, or temperature, of the system:

$$\begin{aligned} & \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \frac{1}{2\pi} \int_{-\infty}^{+\infty} \Theta(t, \omega) dt d\omega \\ &= \frac{1}{2} \sum_{i=1}^N m_i \{ \langle v_{xi}^2 \rangle + \langle v_{yi}^2 \rangle + \langle v_{zi}^2 \rangle \} \\ &= \frac{3}{2} N kT \end{aligned} \quad (7)$$

where k is Boltzmann's constant, T is the temperature, and N is the number of particles.

The Wigner function $\Theta(t, \omega)$ has the undesirable property of not being positive definite, and can experience rapid oscillations as a function of time or frequency. Similar behavior occurs for the quantum mechanical Wigner function. A more useful quantity is the Husimi distribution [10], obtainable from the Wigner function

by local gaussian smoothing. This function is always positive, and is simpler to calculate in practice. In the example described below, we shall employ the Husimi function $\Theta_H(t, \omega)$, defined by:

$$\Theta_H(t, \omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} ds d\mu \Theta(s, \mu) e^{-(s-t)^2/\sigma^2} e^{-\sigma^2(\mu-\omega)^2} \quad (8)$$

where σ is a width parameter determining the relative smoothing windows in frequency and time.

To illustrate the method, we consider a simple example: vibrational relaxation of I_2 in the van der Waals cluster $I_2\text{-Ar}_{13}$ [11]. Our model consists of a pairwise additive potential function, with the dynamics of I_2 in its B electronic state represented by a Morse oscillator [12] and I-Ar and Ar-Ar interactions given by 12-6 Lennard Jones potentials [2]. A minimum energy geometry of the cluster was obtained by quenching a high energy trajectory, resulting in the I_2 impurity embedded in an incomplete solvation shell of argon atoms. The cluster was then equilibrated to an energy corresponding to a time-averaged kinetic energy of 3 K. At $t = 0$, the relative momentum of the I atoms was boosted to correspond to the $v = 20$ quantum state, and Hamilton's equations were integrated for 300 psec.

Figure 1 shows $\Theta_H(t, \omega)$ calculated for a trajectory of the $I_2\text{-Ar}_{13}$ system. The horizontal axis gives the frequency ω in wavenumbers, while the vertical axis gives both the value of $\Theta_H(t, \omega)$ (in arbitrary units) and the time at which the spectrum is calculated (in psec.) Time increases with increasing vertical shift of the spectra. The Figure reveals a large peak centered at 100 cm^{-1} at the beginning of the simulation, with very little intensity at frequencies below 50 cm^{-1} . The large peak is due to the vibrations of the I_2 molecule. It is shifted from the harmonic value of 128 cm^{-1} by the anharmonicity present at $v = 20$, which also results in a second small overtone

appearing at 200 cm^{-1} . The initial absence of low frequency intensity is due to the lack of significant motion of the cold argon atoms. As time progresses, the spectrum evolves: (1) the frequency of the I_2 vibration increases with time, reaching about 120 cm^{-1} by the end of the simulation, (2) the intensity of the high I_2 frequency decreases, and (3) the intensity for low frequencies increases with time. These effects arise due to vibrational relaxation of the initially excited I_2 molecule, with energy flow into the low frequency interatomic degrees of freedom. The I_2 frequency increases with decreasing diatomic energy, due to the anharmonicity of the Morse potential.

In Fig. 2, we investigate the dynamics of energy redistribution in the system by defining two new temperature-like quantities, corresponding to low and high frequency components of the motion:

$$K_{low}(t) = \frac{1}{2\pi} \int_0^{\omega_c} \Theta_H(t, \omega) d\omega \quad (9)$$

$$K_{high}(t) = \frac{1}{2\pi} \int_{\omega_c}^{\infty} \Theta_H(t, \omega) d\omega \quad (10)$$

We take $\omega_c = 75 \text{ cm}^{-1}$, a frequency that divides argon cluster and I_2 impurity contributions to Θ_H . These quantities measure the distribution of energy between low and high frequency degrees of freedom. The solid curve labeled (a) shows the time dependence of K_{high} , while the long-dashed curve (b) gives K_{low} . In addition, we plot the sum $K_{tot} = K_{high} + K_{low}$ as the short-dashed curve (c). K_{tot} is equivalent to a short time average of the instantaneous kinetic energy with a gaussian weighting function. The total is approximately constant with time, while the decrease in K_{high} and concomitant increase in K_{low} indicates vibrational energy

relaxation from the initially excited I_2 into the cluster degrees of freedom. This approach can be generalized to monitor the flow of energy between "modes" defined in frequency space; this model-independent analysis of energy redistribution has advantages in highly nonlinear systems such as this, where, except for the I_2 vibrational degree of freedom, a good set of zeroth order modes are not known.

Insight into I_2 vibrational energy relaxation and its effect on cluster structure and dynamics can be gained from more detailed analysis of the time and frequency dependence of Eq. (8). In Fig. 3 (a) shows the hyperspherical radius of the system, defined as $\rho = [r_1^2 + r_2^2 + \dots + r_{15}^2]^{1/2}$, where r_i is the distance of the i^{th} particle from the cluster center of mass. This quantity provides a useful diagnostic, allowing structural changes of the system to be detected easily. Energy flow from the I_2 impurity into the cluster induces isomerizations, with the promotion of argon atoms from their minimum potential sites across activation barriers to regions of higher potential energy. Similar behavior in pure rare gas clusters and other systems has been interpreted as a finite system analogue of a solid-liquid phase transition [13]. This behavior appears as sudden increases in the hyperspherical radius of the system, such as at $t = 50, 80$, and 130 psec. in Fig. 3 (a). In Fig. 3 (b) we show the corresponding time evolution of the zero frequency component of Θ_H . The structural changes in the system indicated by the time dependence of $\rho(t)$ correlate well with peaks in $\Theta_H(t, \omega=0)$. These peaks are caused by transient aperiodic motion, and occur when the system is in the process of undergoing a structural change—in other words, when transition states are being traversed. For early times, the cluster modes are still relatively cold, and the system migrates from one solid-like configuration to another. This is reflected in the return of $\Theta_H(t, \omega=0)$ to nearly zero, as seen for times less than 150 psec. As the argon degrees of freedom gain energy, $\Theta_H(t, \omega=0)$ experiences an overall increase with superimposed fluctuations.

This corresponds to the onset of diffusive motion in the now fluxional, or liquid, cluster [13].

In summary, the nonstationary time series approach to the analysis of molecular dynamics described here provides a powerful tool for reducing the wealth of data generated by computer simulation into an understandable and physically intuitive form. The gaussian smoothed time-frequency Wigner function $\Theta_H(t, \omega)$, which can be interpreted as a time- and frequency-dependent effective temperature, provides a clear view of the dynamical processes occurring vibrational relaxation in a model $I_2\text{-Ar}_{13}$ system. The approach provides a powerful tool for unraveling the processes occurring in more complicated systems, such as large polyatomic molecules, van der Waals clusters, polymers, and solids. Application to these problems will be described elsewhere [14].

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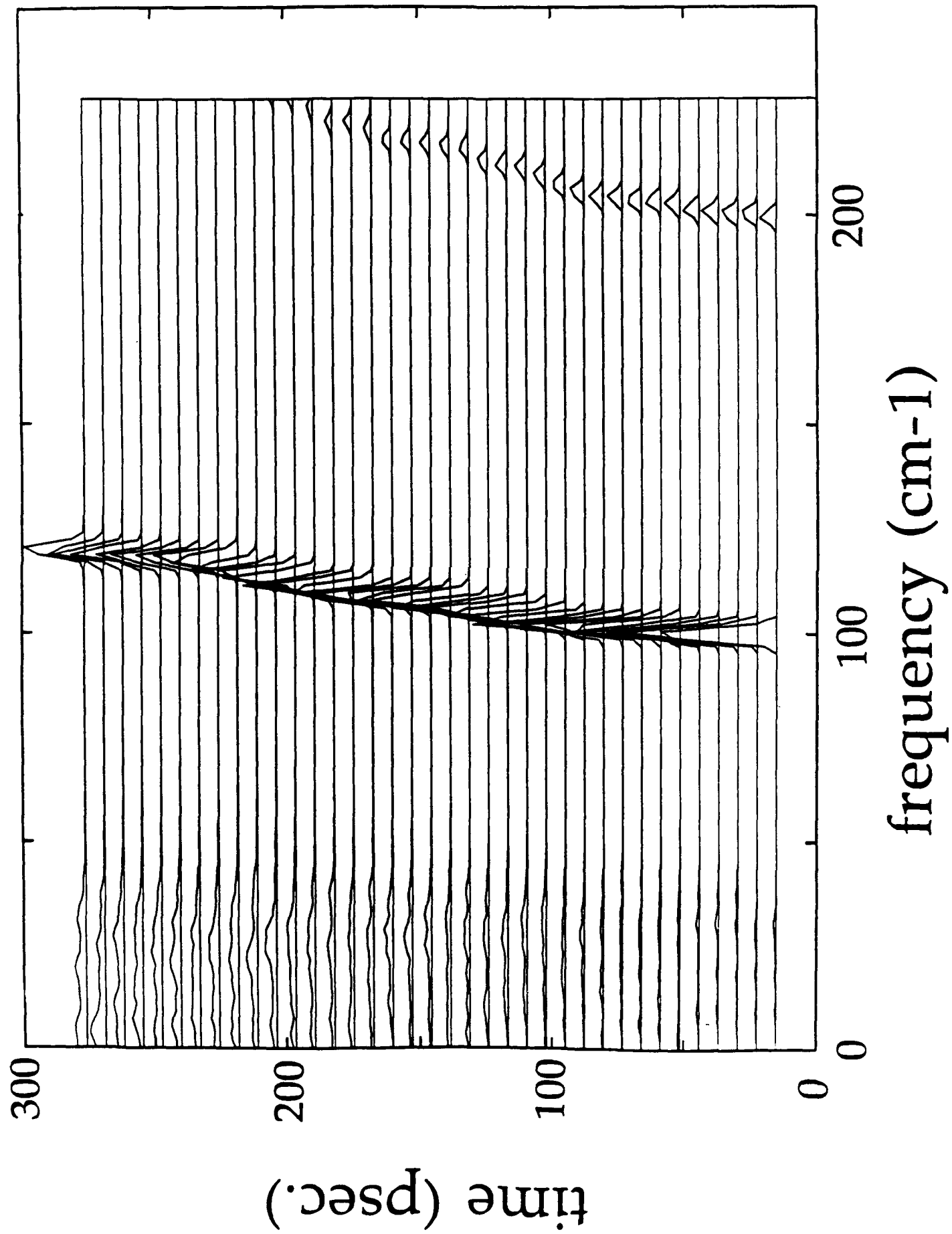
References

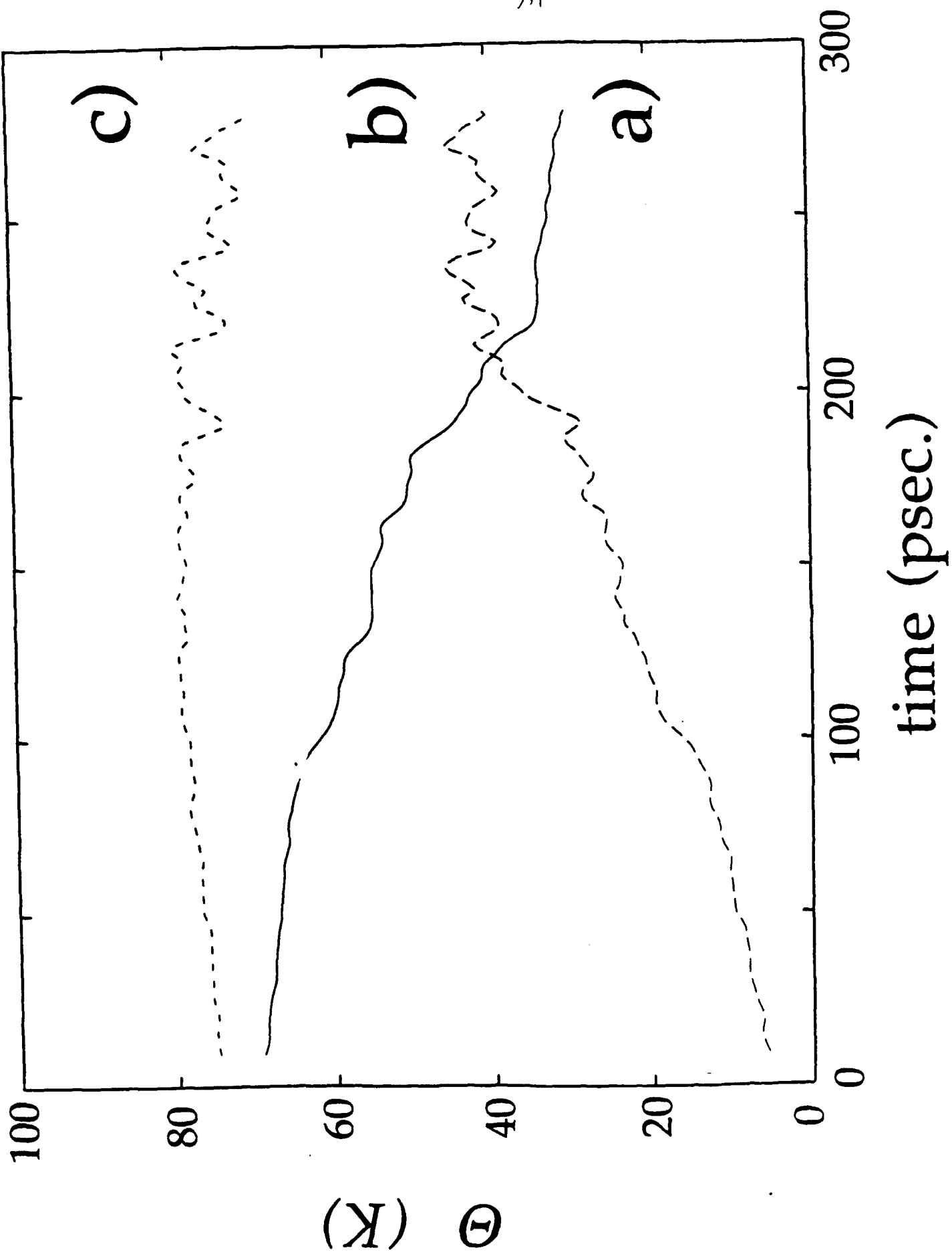
- [1] R.D. Levine and R.B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity* (Oxford, 1987); L. M. Raff and D. L. Thompson, in *Theory of Chemical Reaction Dynamics*, edited by M. Baer (CRC, Boca Raton, 1985).
- [2] *Simulation of Liquids and Solids*, edited by G. Ciccotti, D. Frenkel, and I. R. McDonald (North Holland, NY, 1987); M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).
- [3] D.A. McQuarrie, *Statistical Mechanics* (Harper and Row, New York, 1976).
- [4] See, for example: E. L. Sibert III, W. P. Reinhardt, and J. T. Hynes, *J. Chem. Phys.* **81**, 1115, 1135 (1984); M. J. Davis, *J. Chem. Phys.* **83**, 1016 (1985); J.M. J. Davis and S. K Gray, *J. Chem. Phys.* **84**, 5389 (1986).
- [5] C. C. Martens, M. J. Davis, and G. S. Ezra, *Chem. Phys. Lett.* **142**, 519 (1987).
- [6] See, for example: A. Fendt, S. F. Fischer, and W. Kaiser, *Chem. Phys.* **57**, 55 (1981); H. Graener, T. Q. Ye, and A. Laubereau, *J. Chem. Phys.* **91**, 1043 (1989); J. R. Ambroseo and R. M. Hochstrasser, *J. Chem. Phys.* **89**, 5956 (1988).
- [7] M.B. Priestley, *Spectral Analysis and Time Series* (Academic Press, New York, 1981); L. Cohen and C.A. Pickover, *Proc. IEEE* (1986); *Wavelets*, J.M. Combes, et al. (eds.) (Springer, Berlin, 1989).

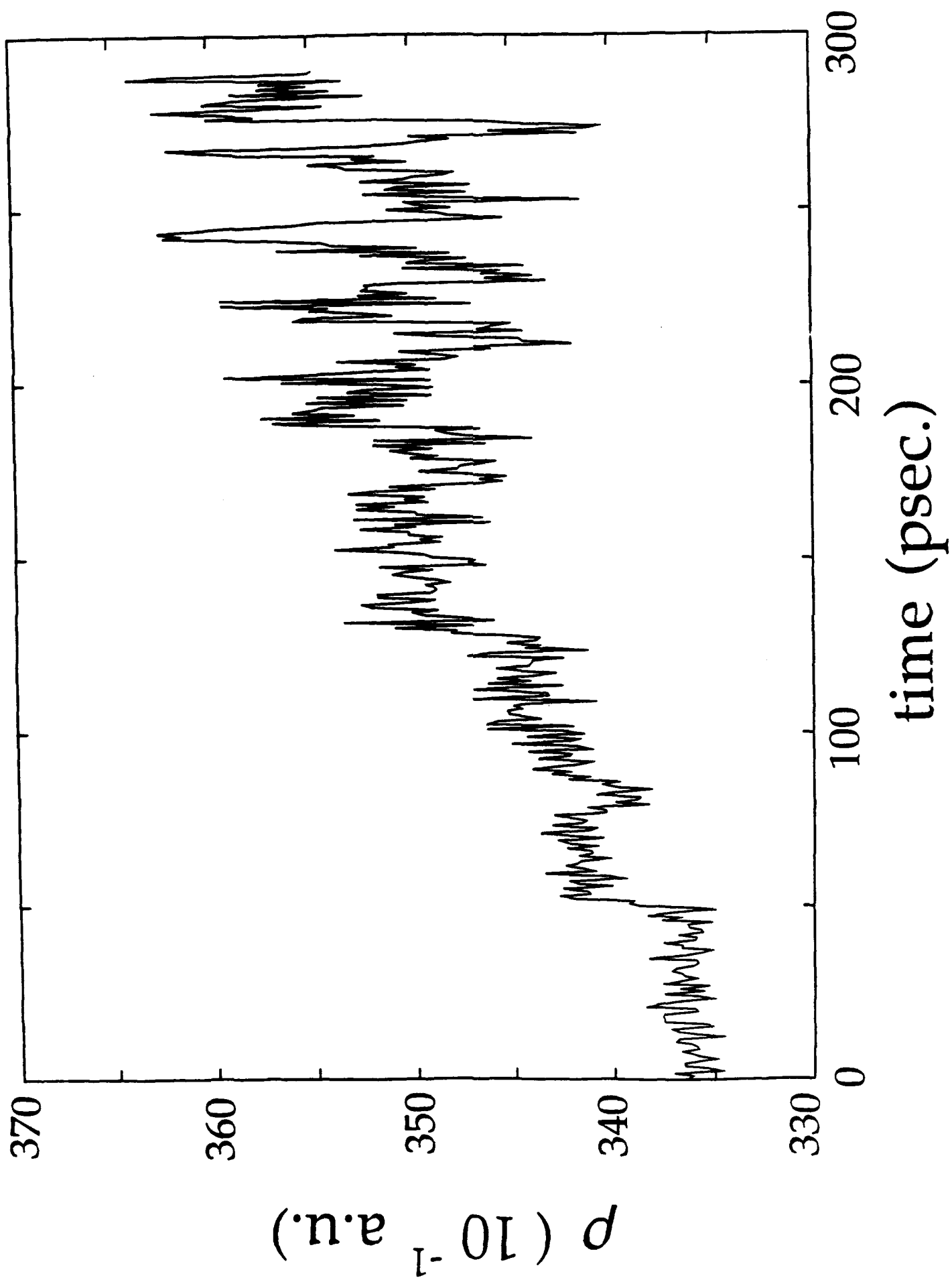
- [8] For applications to chemical physics, see J. D. McDonald and R. A. Marcus, J. Chem. Phys. **65**, 2180 (1976); R. Roy, B. G. Sumpter, G. A. Pfeffer, S. K. Gray, and D. W. Noid, Phys. Reports. **205**, 111 (1991).
- [9] E. P. Wigner Phys. Rev. **40**, 749 (1932).
- [10] K. Husimi, Proc. Phys. Math. Soc. Japan, **22**, 264 (1940).
- [11] For previous simulations of vibrational relaxation of diatomic species in rare gas clusters, see for example: F. G. Amar and B. J. Berne, J. Phys. Chem. **88**, 6720 (1984); D. Scharf, J. Jortner, and U. Landman, J. Chem. Phys. **88**, 4273 (1988).
- [12] J. A. Beswick, G. Delgado-Barrio, and J. Jortner, J. Chem. Phys. **70**, 3895 (1979); S. K. Gray, S. A. Rice, and D. W. Noid, J. Chem. Phys. **84**, 3745 (1986).
- [13] J.D. Honeycutt and H.C. Andersen, J. Phys. Chem. **91**, 4950 (1987); T.L. Beck and R.S. Berry, J. Chem. Phys. **88**, 3910 (1988); T. L. Beck, D. M. Leitner, and R. S. Berry, J. Chem. Phys. **89**, 1681 (1988); P. LaBastie and R.L. Whetten, Phys. Rev. Lett. **65**, 1567 (1990).
- [14] C. C. Martens, in preparation.

Figure Captions

- Figure 1 The time- and frequency- dependent distribution $\Theta_H(t,\omega)$ for I_2 relaxation in Ar_{13} . Horizontal axis shows the frequency in wavenumbers, while the vertical axis gives both the value of $\Theta_H(t,\omega)$ and the time at which the spectra were calculated.
- Figure 2 High frequency (a), low frequency (b), and total integral of $\Theta_H(t,\omega)$ over frequency. See text for discussion.
- Figure 3 (a) hyperspherical radius $\rho(t)$ vs. time for I_2 - Ar_{13} cluster. (b) zero frequency component of $\Theta_H(t,\omega)$. See text for details.







$\Theta(t, \omega=0)$ (arbitrary)

0

100

200

300

time (psec.)

91

16